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FULL PAPER

Preparation and characterization of palladium and platinum complexes bearing 1,8-bis[(diphenylphosphino)methyl]naphthalene

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Reaction of $MCl_2(cod)$ (M = Pd, Pt) with 1,8-bis[(diphenylphosphino)methyl]naphthalene (1,8-dpmn) gave MCl_2(1,8-dpmn) **1** (M = Pd), **2** (M = Pt), as confirmed by X-ray analyses. Complex **1** reacted with xylyl isocyanide **a** (XylNC) in the presence of $NaPF_6$ to give $[Pd(1,8\text{-dpmn})(XylNC)_2](PF_6)_2$ **3a**. Reactions of dinuclear complexes $[M_2(RNC)_6](PF_6)_2$ (**4**: M = Pd, **5**: M = Pt; R = Xyl (**a**) or 2,4,6-$Me_3C_6H_2$ (**b**) (Mes)) with one or two equiv. of 1,8-dpmn gave $[M_2(1,8\text{-dpmn})(RNC)_4](PF_6)_2$ **6** (M = Pd) and **7** (M = Pt), or $[M_2(1,8\text{-dpmn})_2(RNC)_2](PF_6)_2$ **8** (M = Pd) and **9** (M = Pt). The structures of **6b**, **7b** and **8b** were confirmed by X-ray analyses. Reaction of $[Pd_2Cl_2(XylNC)_4]$ with two equiv. of 1,8-dpmn in the presence of $NaPF_6$ gave **8a**, whereas the reaction in the presence of NH_4PF_6 produced **10a** together with **7a**. It was confirmed by an X-ray analysis of **10a** that the crystal lattice is constructed by two types of cations (**3a** and two 2,2,6,6-tetramethyl-4-piperidonium) and four PF_6 anions. Photochemical reaction of **6a** or **8a** in CH_2Cl_2 led to cleavage of the Pd–Pd bond, giving $[PdCl(XylNC)_3](PF_6)$ and $[PdCl(1,8\text{-dpmn})(XylNC)](PF_6)$.

Introduction

1,8-Bis(diphenylphosphino)naphthalene (1,8-dppn) and its derivatives are rigid in their manner of co-ordination because of the direct binding of the phosphorus atoms to the naphthalene rings, and form chelate complexes, MCl_2(1,8-dppn) (M = Pd, Pt).[1,2] 1,8-Bis[(diphenylphosphino)methyl]naphthalene (1,8-dpmn), formed by introduction of a methylene group between the naphthalene ring and phosphorus atom, is less rigid than 1,8-dppn and has the potential for co-ordination modes other than chelation.

We have studied the electrochemical or chemical preparation of di-, tri-, and poly-nuclear platinum and palladium complexes of isocyanides bearing various diphosphines[3–11] or triphosphine.[12] Controlled potential electrolysis of $[Pt(diphos)(RNC)_2]^{2+}$ at a mercury-pool electrode gave $[Pt_2(diphos)_2(RNC)_2]^{2+}$(diphos = $Ph_2(CH_2)_nPPh_2$ (n = 2–4); R = 2,6-$Me_2C_6H_3$ (Xyl), 2,4,6-$Me_3C_6H_2$ (Mes)), $[Pt_2(\mu\text{-dppm})_2(RNC)_2]^{2+}$, $[Pt_3(\mu\text{-dppm})_2(RNC)_4]^{2+}$ (A-frame) and $[HgPt_6(dppb)_2(RNC)_8]$, depending on the coulometric conditions or diphosphines. One-electron reduction of $[Pd(diphos)(RNC)_2]^{2+}$ (diphos = $Ph_2(CH_2)_nPPh_2$, n = 2–4) at a platinum electrode formed the chelate dimers $[Pd_2(diphos)_2(RNC)_2]^{2+}$.[6] Chemical reduction of $[Pt(dpphex)(RNC)_2]^{2+}$ (dpphex = $Ph_2P(CH)_6PPh_2$) with Na/Hg also gave the Pt–Hg mixed cluster $[Hg_2Pt_6(dpphex)_3(RNC)_6]$.[5] These complexes could be prepared by the substitution reactions of $[M_2(RNC)_4]^{2+}$ (M = Pd, Pt) or $[Pt_3(RNC)_8]^{2+}$ with appropriate diphosphines.

We report here the preparations and characterization of four-co-ordinate palladium and platinum complexes bearing 1,8-dpmn. The chemistry of metal complexes bearing 1,8-dpmn is limited to the synthesis of ruthenium complexes of 1,8-dpmn by Tin *et al.*[13]

Results and discussion

Reactions of $MCl_2(cod)$ (M = Pd, Pt) with 1,8-dpmn gave MCl_2(1,8-dpmn) (**1**: M = Pd, **2**: M = Pt) in good yields. X-Ray analyses of **1** and **2** were undertaken. The perspective drawings of **1** and **2** with the atomic numbering schemes are given in Figs. 1 and 2. Selected bond lengths and angles are listed in Table 1. Complexes **1** and **2** are isomorphous. The molecules have *cis* structures with bite angles (P–M–P) of 93.5° for **1** and 94.4° for **2**, compared with those of $RuH_2(CO)(PPh_3)$(1,8-dpmn) (95.96°)[13] and dppb ($Ph_2P(CH_2)_4PPh_2$) complexes (94.51°).[14] The dihedral angles between the MP_2Cl_2 plane and the naphthalene ring are 89.0° for **1** and 86.5° for **2**, respectively. The MP_2Cl_2 plane is also perpendicular to two phenyl rings among four phenyl rings (86–88°). The average Pt–P bond length of 2.236 Å is shorter than the average Pd–P length of 2.263 Å,

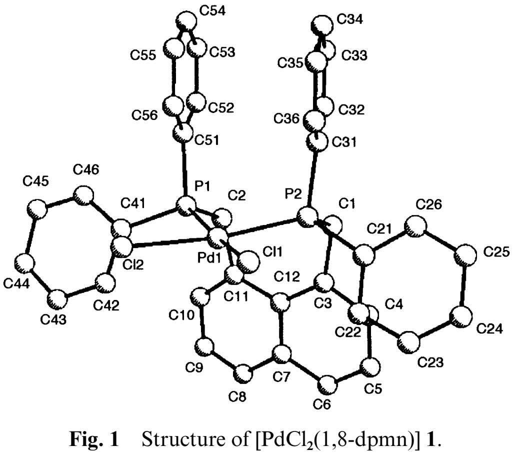

Fig. 1 Structure of $[PdCl_2(1,8\text{-dpmn})]$ **1**.

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Table 1 Selected bond lengths (Å) and angles (°) for *cis*-$PdCl_2$(1,8-dpmn) **1** and *cis*-$PtCl_2$(1,8-dpmn) **2**

(a) *cis*-$PdCl_2$(1,8-dpmn) **1**					
Pd(1)–Cl(1)	2.358(5)	Pd(1)–Cl(2)	2.346(5)	Pd(1)–P(1)	2.261(6)
Pd(1)–P(2)	2.268(5)	P(1)–C(2)	1.86(2)	P(2)–C(1)	1.87(2)
C(1)–C(3)	1.53(2)	C(2)–C(11)	1.51(2)		
Cl(1)–Pd(1)–Cl(2)	88.4(2)	Cl(1)–Pd(1)–P(1)	171.8(2)	Cl(1)–Pd(1)–P(2)	88.4(2)
Cl(2)–Pd(1)–P(1)	88.2(2)	Cl(2)–Pd(1)–P(2)	171.2(2)	P(1)–Pd(1)–P(2)	93.5(2)
Pd(1)–P(1)–C(2)	122.1(6)	Pd(1)–P(2)–C(1)	122.9(6)	P(2)–C(1)–C(3)	111(1)
P(1)–C(2)–C(11)	115(1)				
(b) *cis*-$PtCl_2$(1,8-dpmn) **2**					
Pt(1)–Cl(1)	2.355(7)	Pt(1)–Cl(2)	2.353(7)	Pt(1)–P(1)	2.234(7)
Pt(1)–P(2)	2.238(7)	P(1)–C(1)	1.86(3)	P(2)–C(2)	1.81(3)
C(1)–C(3)	1.49(3)	C(2)–C(11)	1.55(3)		
Cl(1)–Pt(1)–Cl(2)	86.3(3)	Cl(1)–Pt(1)–P(2)	89.3(3)	Cl(1)–Pt(1)–P(1)	171.9(3)
Cl(2)–Pt(1)–P(1)	89.0(3)	Cl(2)–Pt(1)–P(2)	171.4(3)	P(1)–Pt(1)–P(2)	94.4(3)
Pt(1)–P(1)–C(1)	120.8(9)	Pt(1)–P(2)–C(2)	120(1)	P(1)–C(1)–C(3)	119(2)
P(2)–C(2)–C(11)	115(2)				

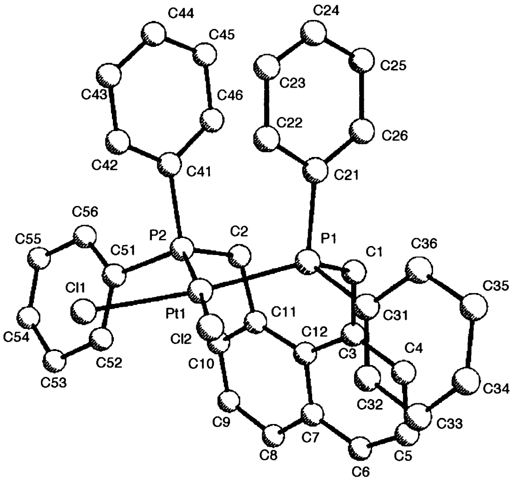
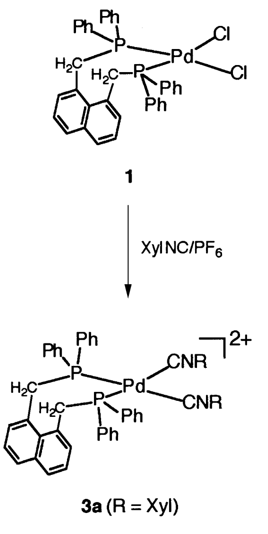


Fig. 2 Structure of [$PtCl_2$(1,8-dpmn)] **2**.



Scheme 1 Reaction of *cis*-$PdCl_2$(1,8-dpmn) **1** with xylyl isocyanide in the presence of $NaPF_6$. The PF_6 anions are omitted for clarity.

whereas the average M–Cl bond lengths for Pd and Pt complexes are identical.

Complex **1** was treated with xylyl isocyanide (XylNC) in the presence of $NaPF_6$ at room temperature to give [Pd(1,8-dpmn)(XylNC)$_2$](PF_6)$_2$ **3a** in high yield (Scheme 1). The IR spectrum showed a characteristic band at 2213 cm^{-1}, corresponding to the terminal isocyanide groups.

When dimeric palladium or platinum complexes [M_2(RNC)$_6$](PF_6)$_2$ (**4**: M = Pd, **5**: M = Pt; **a**: R = Xyl, **b**: R = Mes) were treated with an equiv. of 1,8-dpmn, yellow crystals formulated as [M_2(1,8-dpmn)(RNC)$_4$](PF_6)$_2$ (**6**: M = Pd; **7**: M = Pt) were formed (Scheme 2). The IR spectra of **6** and **7** showed a strong band at *ca.* 2165 cm^{-1} and a very weak band at *ca.* 2190 cm^{-1}, due to the N–C triple bond. The ^1H NMR spectra of **6** and **7** showed the presence of four kinds of isocyanide ligands, suggesting that all isocyanide ligands are nonequivalent. The $^{31}P\{^1H\}$ NMR spectra of **6** showed a doublet around δ 21 and 13 with $^2J_{PP'}$ = 54.5 Hz, respectively; the former is assignable to the phosphorus atom in a *trans*-position to the Pd atom and the latter to that in a *cis*-position, based on the chemical shift in the $^{31}P\{^1H\}$ NMR spectrum of [Pt_2(1,8-dpmn)(RNC)$_4$](PF_6)$_2$ (*vide infra*).

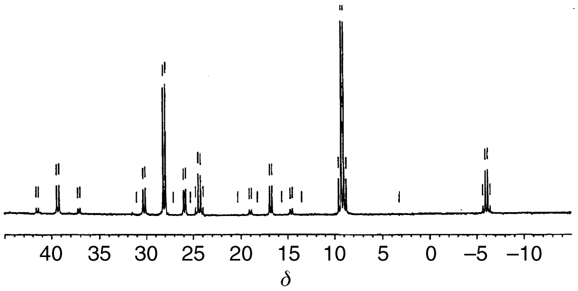
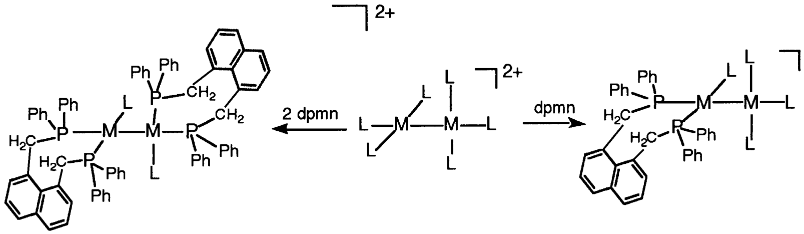


Fig. 3 The $^{31}P\{^1H\}$ NMR spectrum of **7a**.

The $^{31}P\{^1H\}$ NMR spectrum of [Pt_2(1,8-dpmn)(XylNC)$_4$](PF_6)$_2$ **7a** indicated two sets of resonances centered at δ 28.0 and 9.2, which are accompanied by satellite peaks due to ^{195}Pt (I = 1/2) atom (Fig. 3). The observed spectrum is explicable as a combination of four isotopomers, P_2Pt–Pt, P_2Pt–^{195}Pt, $P_2{}^{195}Pt$–Pt and $P_2{}^{195}Pt$–^{195}Pt (their ratios calculated from the natural abundance are 4 : 2 : 2 : 1). From the higher field set (A) centered at δ 9.2, the values of $^1J_{PPt}$, $^2J_{PPt}$ and $^2J_{PP'}$ were estimated to be 3076, 53 and 25 Hz, respectively. From the lower field set (B) centered at δ 28.0, the values of $^1J_{P'Pt}$, $^2J_{P'Pt}$ and $^2J_{PP'}$ were estimated to be 2275, 440 and 25 Hz, respectively. From analogy to the $^{31}P\{^1H\}$ NMR spectra of [Pt_2(diphos)$_2$(RNC)$_2$](PF_6)$_2$ bearing the chelate structure and comparison with the values of the $^2J_{PPt}$ coupling constants, the resonance A was assigned to the phosphorus atom occupying the position *cis* to the Pt–Pt bond and the resonance B, to the phosphorus atom in the *trans* position to the Pt–Pt bond. A similar pattern was observed in **7b**.

X-Ray crystallographic analyses of **6b** and **7b** were undertaken. The perspective drawings of the complex cations of **6b** and **7b** with the atomic numbering schemes are given in Figs. 4 and 5. Some selected bond lengths and angles are listed in Table 2. The complex cations consist of two palladium or platinum atoms joined by a metal–metal σ-bond. The Pd(2) or Pt(2) atom



8 (M = Pd); **9** (M = Pt)

4: M = Pd; **5**: M = Pt
a: L = XylNC; **b**: L = MesNC

6: M = Pd; **7**: M = Pt

Scheme 2 Reaction of $[M_2(RNC)_4](PF_6)_2$ (M = Pd, Pt) with 1,8-dpmn. The PF_6 anions are omitted for clarity.

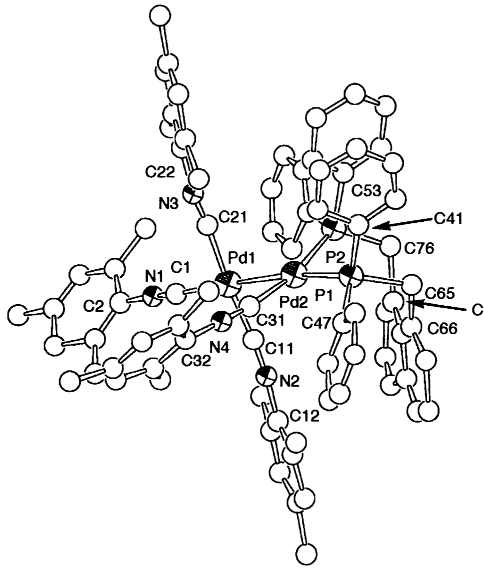


Fig. 4 Structure of $[Pd_2(1,8\text{-dpmn})(MesNC)_4](PF_6)_2$ **6b**. The PF_6 anions are omitted for clarity.

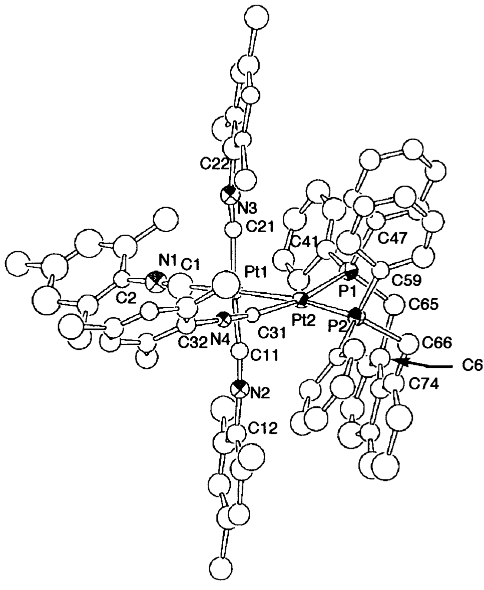


Fig. 5 Structure of $[Pt_2(1,8\text{-dpmn})(MesNC)_4](PF_6)_2$ **7b**. The PF_6 anions are omitted for clarity.

is co-ordinated by two phosphorus atoms of a bidentate 1,8-dpmn ligand, a terminal carbon atom of isocyanide and another Pd(1) or Pt(1) atom, which is surrounded by the terminal carbon atoms of three isocyanide ligands. The structures are in good agreement with the nonequivalence of isocyanide ligands in the ^1H NMR spectra.

A dihedral angle between the $[MP_2C]$ and $[MC_3]$ co-ordination planes is 99(1)° for **6b** and 83(1)° for **7b**, nearly perpendicular as observed in other dinuclear complexes, minimizing the repulsion between the ligands. Similar structures have been observed in the nonbridged dimer.

The naphthalene ring has a dihedral angle of 69(1)° for the Pd(2)P(1)P(2)C(31) plane compared to 108(1)° for the Pt(2)P(1)P(2)C(31) plane. The Pd(1)–Pd(2) (2.568(3) Å) and Pt(1)–Pt(2) (2.61(4) Å) bond lengths are significantly longer than those for isocyanide dimers without phosphine ligands, $[Pd_2Cl_2(^tBuNC)_4]$ (2.532(2) Å),[15] $[Pd_2(MeNC)_6](PF_6)_2$ (2.531(1) Å),[16–18] $[Pd_2I_2(MeNC)_4]$ (2.533(1) Å)[19] and $[Pt_2Cl_2(2,4\text{-}^tBu_2\text{-}6\text{-}MeC_6H_2NC)_4]$ (2.532(2) Å).[20] The Pd(2)–P(1) bond length of 2.351(7) Å and Pt(2)–P(2) bond length of 2.39(4) Å in a *trans*-position to the metal atom are longer than those found in another M–P bond in a *cis*-position, due to the strong *trans*-influence of the metal–metal bond. The P–M–P bite angles for both complexes are typical. The average M(2)–M(1)–C bond angles in the $M(1)C_3$ plane are 84° for both **6b** and **7b** and the M(1)–M(2)–C(31) angles in the $M(2)P_2C(31)$ plane are 72.8(10)° for **6b** and 80(1)° for **7b**. Each isocyanide ligand is bent toward another metal atom. The large inward bend of the latter depends on the steric bulk of the diphosphine. This trend has been noted in $[M_2(diphos)_2(RNC)_2](PF_6)_2$ (M = Pd,[9] Pt[10]). The M–C–N and C–N–C bond angles, except Pt(1)–C(1)–N(1) (165(4)°), C(1)–N(1)–C(2) (166(4)°) and C(11)–N(2)–C(12) (167(4)°), are linear (171–179°).

When the reactions between $[M_2(RNC)_8](PF_6)_2$ and 1,8-dpmn were carried out in a 1 : 2 molar ratio, further substitution reactions occurred to form $[M_2(1,8\text{-dpmn})_2(RNC)_2](PF_6)_2$ (**8**: M = Pd; **a**: R = Xyl; **b**: R = Mes. **9**: M = Pt; **a**: R = Xyl; **b**: R = Mes) (Scheme 2). The IR spectra showed the band due to the terminal isocyanide groups at *ca.* 2130 cm^{-1}. It is reasonable, given the high electron donation ability of diphosphines, that the $\nu(N{\equiv}C)$ frequency is shifted to *ca.* 30 cm^{-1} lower energy than for the monochelate complexes **6** and **7**. The ^1H NMR spectra of **8** and **9** showed the presence of only one type of isocyanide ligand.

The $^{31}P\{^1H\}$ NMR spectra of **8** showed two sets of resonances at δ *ca.* 9.0 and 20.0. The $^{31}P\{^1H\}$ NMR spectrum of **8b** has been satisfactorily simulated using a computer analysis based on a AA′XX′ spin system. The observed and calculated $^{31}P\{^1H\}$ NMR spectrum for **8b** is depicted in Fig. 6, but attempts to simulate the spectrum **8a** were unsuccessful due to spectral overlapping. Analogously, the analyses of the $^{31}P\{^1H\}$ NMR spectra of **9** were unsuccessful because of the very complicated patterns.

A structure of the complex cation of **8b** with the atomic numbering scheme is given in Fig. 7. Selected bond lengths and angles are listed in Table 3. The molecule has a crystallographically imposed inversion center in the middle of the Pd···Pd* vector. The complex cation consists of two palladium atoms joined by a Pd–Pd σ-bond. Each palladium atom is surrounded by two phosphorus atoms from the bidentate 1,8-dpmn ligand, a terminal carbon atom from the isocyanide, and another palladium atom in a nearly planar array. The dihedral angle between two $[PdP_2C]$ co-ordination planes is 79.8°, being smaller by 6° than those of $[Pd_2(MesNC)_2(dppp)_2](PF_6)_2$ (86°)[9] and $[Pt_2(MesNC)_2(dppp)_2](PF_6)_2$ (86°).

The Pd–Pd bond length of 2.670(3) Å is significantly longer

Table 2 Selected bond lengths (Å) and angles (°) for $[Pd_2(1,8\text{-dpmn})(MesNC)_4](PF_6)_2\cdot(CH_3)_2CO$ **6b**·$(CH_3)_2CO$ and $[Pt_2(1,8\text{-dpmn})(MesNC)_4](PF_6)_2$ **7b**

(a) $[Pd_2(1,8\text{-dpmn})(MesNC)_4](PF_6)_2\cdot(CH_3)_2CO$ **6b**·$(CH_3)_2CO$					
Pd(1)–Pd(2)	2.568(3)	Pd(1)–C(1)	2.07(3)	Pd(1)–C(11)	2.02(2)
Pd(1)–C(21)	1.99(2)	Pd(2)–P(1)	2.351(7)	Pd(2)–P(2)	2.291(8)
Pd(2)–C(31)	1.85(3)	C(1)–N(1)	1.15(3)	C(11)–N(2)	1.12(2)
C(21)–N(3)	1.12(2)	C(31)–N(4)	1.22(3)		
Pd(2)–Pd(1)–C(1)	178.5(6)	Pd(2)–Pd(1)–C(11)	83.6(7)	Pd(2)–Pd(1)–C(21)	84.4(7)
C(1)–Pd(1)–C(11)	94.9(10)	C(1)–Pd(1)–C(21)	97.1(9)	C(11)–Pd(1)–C(21)	167(1)
Pd(1)–Pd(2)–P(1)	171.5(2)	Pd(1)–Pd(2)–P(2)	93.8(2)	Pd(1)–Pd(2)–C(31)	72.8(10)
P(1)–Pd(2)–P(2)	93.2(3)	P(1)–Pd(2)–C(31)	101(1)	P(2)–Pd(2)–C(31)	163.1(9)
Pd(1)–C(1)–N(1)	176(2)	C(1)–N(1)–C(2)	179(2)	Pd(1)–C(11)–N(2)	170(2)
C(11)–N(2)–C(12)	172(3)	Pd(1)–C(21)–N(3)	178(2)	C(21)–N(3)–C(22)	175(2)
Pd(2)–C(31)–N(4)	171(2)	C(31)–N(4)–C(32)	170(2)	P(1)–C(65)–C(66)	109(1)
P(2)–C(76)–C(74)	106(1)				
(b) $[Pt_2(1,8\text{-dpmn})(MesNC)_4](PF_6)_2$ **7b**					
Pt(1)–Pt(2)	2.61(4)	Pt(1)–C(1)	1.97(6)	Pt(1)–C(11)	1.83(3)
Pt(1)–C(21)	1.99(3)	Pt(2)–P(1)	2.24(4)	Pt(2)–P(2)	2.39(4)
Pt(2)–C(31)	2.03(5)	C(1)–N(1)	1.08(7)	C(11)–N(2)	1.22(3)
C(21)–N(3)	1.13(3)	C(31)–N(4)	1.17(5)		
Pt(2)–Pt(1)–C(1)	176(1)	Pt(2)–Pt(1)–C(11)	84(1)	Pt(2)–Pt(1)–C(21)	84(1)
C(1)–Pt(1)–C(11)	93(1)	C(1)–Pt(1)–C(21)	97(1)	C(11)–Pt(1)–C(21)	167(2)
Pt(1)Pt(2)–P(1)	94(1)	Pt(1)–Pt(2)–P(2)	171(1)	Pt(1)–Pt(2)–C(31)	80(1)
P(1)–Pt(2)–P(2)	93.3(10)	P(1)–Pt(2)–C(31)	168.7(8)	P(2)–Pt(2)–C(31)	92(1)
Pt(1)–C(1)–N(1)	165(4)	C(1)–N(1)–C(2)	166(4)	Pt(1)–C(11)–N(2)	175(2)
C(11)–N(2)–C(12)	167(4)	Pt(1)–C(21)–N(3)	175(4)	C(21)–N(3)–C(22)	171(3)
Pt(1)–C(31)–N(4)	173(2)	C(31)–N(4)–C(32)	172(4)	P(1)–C(65)–C(67)	112(2)
P(2)–C(66)–C(74)	106(2)				

Table 3 Selected bond lengths (Å) and angles (°) for $[Pd_2(1,8\text{-dpmn})_2(MesNC)_2](PF_6)_2\cdot(CH_3)_2CO$ **8b**·$2(CH_3)_2CO$

Pd(1)–Pd(2)	2.670(3)	Pd(1)–P(1)	2.330(5)	Pd(1)–P(2)	2.387(5)
Pd(1)–C(1)	1.95(2)	C(1)–N(1)	1.18(2)		
Pd(1)*–Pd(1)–P(1)	103.7(1)	Pd(1)–Pd(1)–P(2)	164.6(1)	Pd(1)*–Pd(1)–C(1)	72.4(5)
P(1)–Pd(1)–P(2)	91.4(2)	P(1)–Pd(1)–C(1)	171.2(5)	P(2)–Pd(1)–C(1)	93.0(5)
Pd(1)–C(1)–N(1)	167(1)	C(1)–N(1)–C(11)	174(2)	P(1)–C(112)–C(109)	109(1)
P(2)–C(111)–C(101)	106(1)				

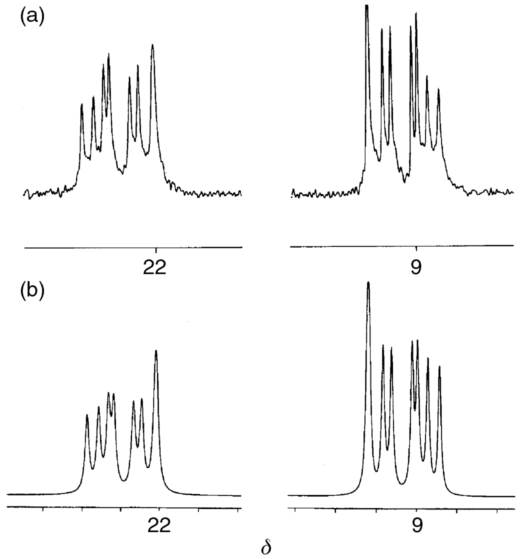


Fig. 6 (a) Observed and (b) calculated $^{31}P\{^1H\}$ NMR spectrum for $[Pd_2(1,8\text{-dpmn})_2(MesNC)_2](PF_6)_2$ **8b**.

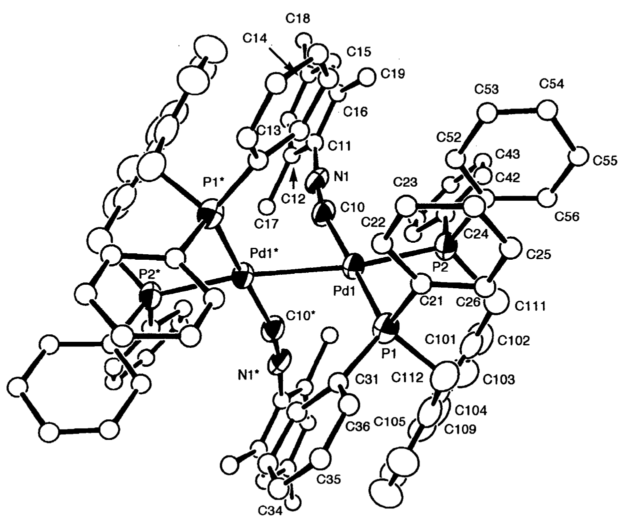


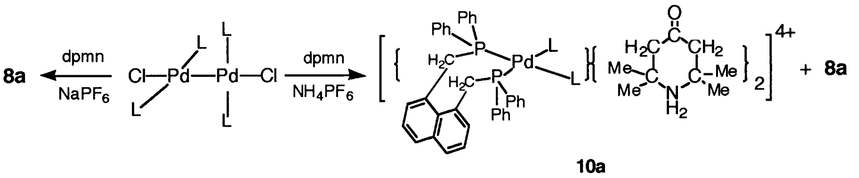
Fig. 7 Structure of $[Pd_2(1,8\text{-dpmn})_2(MesNC)_2](PF_6)_2$ **8b**. The PF_6 anions are omitted for clarity.

than those in the bis-diphosphine complexes, $[Pd_2(MesNC)_2(dppp)_2](PF_6)_2$ (2.617(2) Å)[9] and $[Pd_2(XylNC)_2(dppen)_2](PF_6)_2$ (dppen = $Ph_2PCH{=}CHPPh_2$) (2.602(1) Å)[9] and $[Pd_2(XylNC)_2(dppf)_2](PF_6)_2$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene (2.602(1) Å),[21] probably due to minimization of the steric repulsion between the naphthalene ring and the isocyanide connected to another palladium atom. The average Pd–Pd–P_{ax} angle is 165.3°, comparable to that in $[Pd_2(XylNC)_2(dppf)_2](PF_6)_2$ (163.75°).

The P(1)–Pd(1)–P(2) bite angle of 91.4(2)° is narrower than that of **6b** (93.2(3)°). The Pd(1)*–Pd(1)–C(1) angle of 72.4(5)° is similar to the corresponding angles for **6b** and **7b**. A characteristic feature is that the Pd(1)*–Pd(1)–P(1) angle of 103.7(1)° is wider by *ca.* 10° than those of the mono-substituted diphosphine complexes **6b** and **7b**, minimizing the repulsive

Table 4 Selected bond lengths and angles for $[\{Pd(1,8\text{-}dpmn)(XylNC)_2\}\{HN(CH_2)_2(CMe_2)_2CO\}_2](PF_6)_4$ **10a**

$[Pd(1,8\text{-}dpmn)(XylNC)_2]^{2+}$					
Pd(1)–P(1)	2.312(7)	Pd(2)–P(2)	2.305(8)	Pd(1)–C(37)	1.89(3)
Pd(1)–C(46)	1.96(3)	C(37)–N(1)	1.15(3)	C(46)–N(2)	1.15(3)
P(1)–Pd(1)–P(2)	93.3(3)	P(1)–Pd(1)–C(37)	171.2(9)	P(1)–Pd(1)–C(46)	88.0(7)
P(2)–Pd(1)–C(37)	91.1(9)	P(2)–Pd(1)–C(46)	172.4(8)	C(37)–Pd(1)–C(46)	86(1)
Pd(1)–C(37)–N(1)	175(2)	C(37)–N(1)–C(38)	169(2)	Pd(2)–C(46)–N(2)	176(2)
C(36)–N(2)–C(47)	178(2)	P(1)–C(11)–C(1)	115(1)	P(2)–C(24)–C(9)	110(1)
[2,2,6,6-Tetramethyl-4-piperidonium]					
N(3)–C(57)	1.49(4)	N(3)–C(60)	1.51(4)	C(55)–O(1)	1.29(4)
N(4)–C(66)	1.48(3)	N(4)–C(69)	1.52(4)	C(64)–O(2)	1.11(3)



Scheme 3 Reaction of $[Pd_2Cl_2(XylNC)_4]$ with 1,8-dpmn in the presence of NH_4PF_6 or $NaPF_6$ (L = XylNC). The PF_6 anions are omitted for clarity.

interaction with another 1,8-dpmn ligand. The structure of platinum complex **9** is considered to be similar to that of **8**.

When two equiv. of 1,8-dpmn was added to a CH_2Cl_2 solution of trinuclear complex $[Pd_3(XylNC)_8](PF_6)_2$ at room temperature, the reaction solution changed rapidly from yellow to violet and finally to yellow. This color change suggested the occurrence of a substitution reaction with 1,8-dpmn but attempts to isolate the violet species were unsuccessful because the change proceeded very quickly, suggesting that a trinuclear complex bearing diphosphine is very unstable. This trend has also been observed in the reaction of $[Pd_3(XylNC)_8](PF_6)_2$ with the bulky phosphine, $[2,6\text{-}(MeO)_2C_6H_3)]_3P$.[22]

Reactions of $[Pd_2Cl_2(XylNC)_4]$ with 1,8-dpmn in the presence of $NaPF_6$ or NH_4PF_6

When the neutral dinuclear complex $[Pd_2Cl_2(XylNC)_4]$, was treated in acetone, with two equiv. of 1,8-dpmn in the presence of excess $NaPF_6$, **8a** was obtained. However on treatment with an excess of NH_4PF_6, two complexes, **8a** and **10a** formulated as $[\{Pd(1,8\text{-}dpmn)(XylNC)_2\}\{HN(CH_2)_2(CMe_2)_2CO\}_2](PF_6)_4$, were formed (Scheme 3).

It was confirmed by X-ray analysis that **10a** consists of two kinds of cations, $[Pd(1,8\text{-}dpmn)(XylNC)_2]^{2+}$ and two 2,2,6,6-tetramethyl-4-piperidonium, and four PF_6 anions (Fig. 8 and Table 4). It is very rare that two kinds of cations are incorporated into the crystal lattice. The complex cation, $[Pd(1,8\text{-}dpmn)(XylNC)_2]^{2+}$ was surrounded by two phosphorus atoms of 1,8-dpmn and the terminal carbon atoms of two isocyanide ligands. The dihedral angle between the PdP_2C_2 and naphthalene planes is 104.3°, comparable with that for **7b**. The P(1)–Pd–P(2) bite angle is 93.3(3)°, comparable with those of **1** and **2**. The piperidonium cation adopted a typical chair-form. The bond lengths and angles fall within the usual values.

The IR spectrum of **10a** showed characteristic absorption bands at 3198, 3135, 2218 and 1725 cm^{-1}. The band at *ca.* 2200 cm^{-1} is assigned to terminal isocyanide ligands. Two bands around 3160 cm^{-1} and the bond at 1725 cm^{-1} are due to the N–H and C=O groups, respectively. The presence of PF_6 anions was confirmed by a broad band at 847 cm^{-1}. In the ^1H NMR spectrum, the methyl and methylene protons of the piperidonium cation and *o*-methyl protons of isocyanide appeared at δ 1.69, 2.87 and 1.99, respectively. Multiplets of the P–CH_2 protons appeared at δ *ca.* 4.63 and *ca.* 5.86. The $^{31}P\{^1H\}$ NMR spectrum indicated a singlet at δ 30.3, in close agreement with that of **3a**. After several crystallizations of **10a** **3a** and a piperidonium cation as a PF_6 salt could be isolated separately.

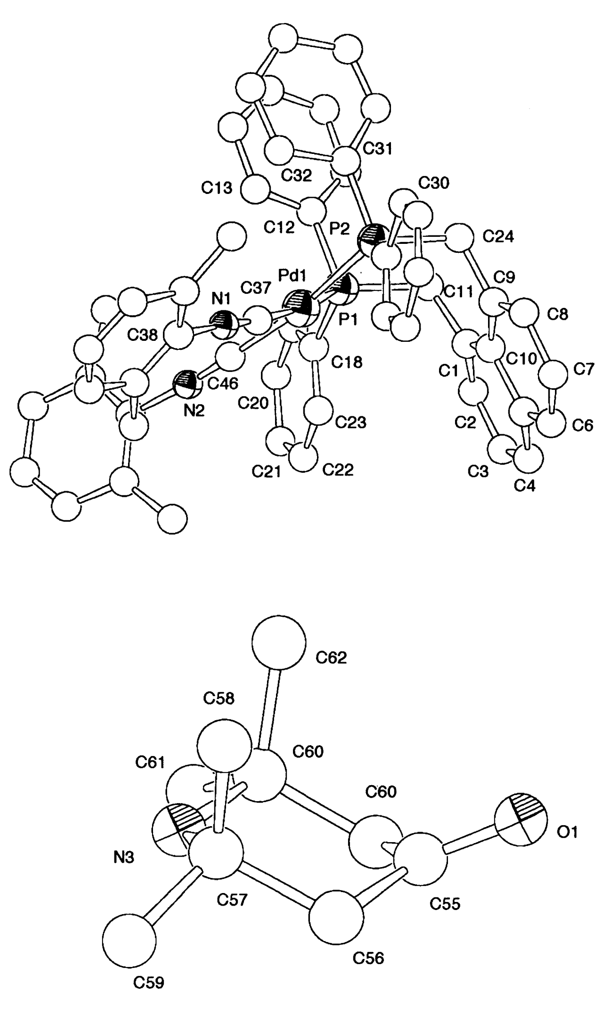
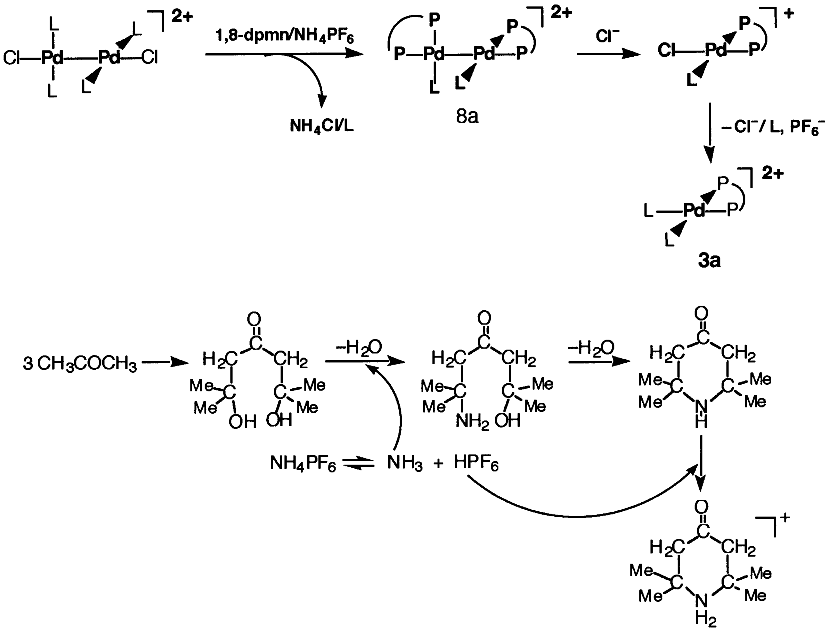


Fig. 8 Structures of two cations, $[Pd(1,8\text{-}dpmn)(XylNC)_2]^{2+}$ and 2,2,6,6-tetramethyl-4-piperidonium in **10a**. The PF_6 anions are omitted for clarity.

Preparation of complex **10a** consists of an initial formation of **8a**, accompanied by cleavage of the metal–metal bond and generation of NH_4Cl as shown in Scheme 4. This mechanism has also been observed in the reaction of $[Pd_2Cl_2(XylNC)_4]$ with tris(2,6-dimethoxyphenyl)phosphine (L) in the presence of NH_4PF_6 to give $[PdCl(L)(XylNC)_2](PF_6)$.[22] Finally, complex **3a**



Scheme 4 A possible path for the formation of **10a**. The PF_6 anions are omitted for clarity. L = XylNC; P⌒P = 1,8-dpmn.

was obtained by the reaction of [PdCl(1,8-dpmn)(XylNC)](PF_6) with xylyl isocyanide. In order to examine the origin of 2,2,6,6-tetramethyl-4-piperidonium, a mixture of NH_4PF_6 and acetone was treated at room temperature for 24 h and led to the formation of a PF_6 salt of 2,2,6,6-tetramethyl-4-piperidonium, [HN(CH_2)$_2$(CMe_2)$_2$CO](PF_6), in high yield, suggesting that the palladium complex is unnecessary for the formation of a piperidonium salt. No piperidonium derivative was obtained when the reaction was carried out for a short time. In fact, a short reaction gave only **8a**. The reaction consists of an amination of NH_3, generated by an equilibrium of NH_4PF_6, to a diol arising from the trimerization of acetone, accompanied by a ring closure (Scheme 4).

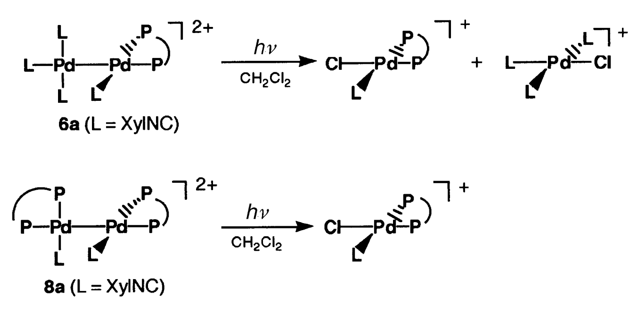
Photochemical reactions of dinuclear palladium complexes

In the UV-vis spectra of **6** and **8**, the lowest energy absorption band appeared at *ca.* 385 nm for **6** and *ca.* 460 nm for **8**, assigned to the $\sigma \rightarrow \sigma^*$ transition of the Pd–Pd bond. It is reasonable, given the high electron-donating ability of diphosphines, that the metal–metal bonds of **8** are weaker than those of **6**. This was traced back to the Pd–Pd bond lengths; the Pd–Pd length is 2.568 Å for **6b** and 2.670 Å for **8b**. The $\sigma \rightarrow \sigma^*$ transitions of [Pd_2(diphos)$_2$(RNC)$_2$](PF_6)$_2$ (diphos = $Ph_2P(CH_2)_nPPh_2$; $n = 2$–4), having a structure similar to **8**, have been observed in the range from 421 to 434 nm,[9] suggesting that 1,8-dpmn is a stronger electron-donating ligand than diphosphines bearing methylene groups, such as dppe, dppp, *etc.* This observation is in agreement with the fact that the bond length of **8b** is longer than that found for [Pd_2{$Ph_2P(CH_2)_3PPh_2$}$_2$(XylNC)$_2$](PF_6)$_2$.

When **6a** was irradiated in CH_2Cl_2, the solution changed from yellow to colorless. The $\sigma \rightarrow \sigma^*$ transition around 385 nm decreased and finally no appreciable absorption was observed in the region $\lambda > 380$ nm. This reaction was monitored spectroscopically, and the formation of two complexes, [PdCl(XylNC)$_3$](PF_6) and [PdCl(1,8-dpmn)(XylNC)](PF_6), was confirmed (Scheme 5). Photochemical reaction of **8a** also showed a similar color-change and cleaved a Pd–Pd bond to give [PdCl(1,8-dpmn)(XylNC)](PF_6). The bond-cleavage rate of **8a** is faster than that of **6a**.

Experimental

All reactions were carried out under a nitrogen atmosphere.



Scheme 5 Photochemical reactions of **6a** and **8a**. The PF_6 anions are omitted for clarity. P⌒P = 1,8-dpmn.

Isocyanides,[23] 1,8-bis(dichloromethyl)naphthalene,[24] [Pd_2Cl_2(RNC)$_4$],[25] [Pd_2(RNC)$_6$](PF_6)$_2$,[20] [Pt_2(RNC)$_6$](PF_6)$_2$,[20] and [Pd_3(RNC)$_8$](PF_6)$_2$[20] were prepared according to the literature. Dichloromethane was distilled over CaH_2 and diethyl ether was distilled over $LiAlH_4$. The IR spectra were measured on an FT/IR-5300 instrument. The ^{1}H NMR spectra were measured at 250 MHz and ^{31}P{^{1}H}-NMR spectra were measured at 101 MHz using 85% H_3PO_4 as an external reference.

Syntheses

Preparation of 1,8-bis[(diphenylphosphino)methyl]naphthalene. Triphenylphosphine (7.6 g, 29.0 mmol) and lithium (0.6 g, 86.5 mmol) in tetrahydrofuran (THF) (40 mL), were stirred for one day at room temperature, and lithium was removed by filtration. *tert*-Butyl chloride (3.4 mL, 31 mmol) in THF (10 mL) was added to the ice cooled solution which was then heated at reflux for 10 min. After cooling in an ice-bath, 1,8-[bis(dichloromethyl)]naphthalene (3.5 g, 15.6 mmol) in THF (40 mL) was added dropwise and the mixture was refluxed for 30 min. The solvent was removed and a mixture of H_2O (200 mL) and Et_2O (200 mL) was added to form white solids. The solids were filtered and washed with EtOH to give 1,8-dpmn (3.0 g, 37%). ^{1}H NMR ($CDCl_3$): δ 4.21 (d, PCH_2, 4H), 6.6–7.7 (c, napthalene, 26H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −11.4 (s). Anal. calc. for $C_{36}H_{30}P_2$: C, 82.43; H, 5.78. Found: C, 82.62; H, 5.55%.

Preparation of $PdCl_2$(1,8-dpmn)·1.5CH_2Cl_2 1·1.5CH_2Cl_2. To a solution of $PdCl_2$(cod) (50 mg, 0.18 mmol) in CH_2Cl_2 (5 mL), 1,8-dpmn (96 mg, 0.18 mmol) in CH_2Cl_2 (10 mL) was added at room temperature. After stirring for 2 h, the mixture was filtered on a glass filter (G4) and the solvent was concentrated to *ca.* 3 mL and diethyl ether was added to give pale yellow crystals of **1**$\cdot 1.5CH_2Cl_2$ (112 m, 77%). ^1H NMR ($CDCl_3$): δ 4.97 (d, $J_{PH} = 11.3$ Hz, 4H, CH_2), 5.27 (s, CH_2Cl_2), 7.02–7.93 (m, 26H, napthalene). ^{31}P NMR ($CDCl_3$): δ 33.4. Anal. calc. for $C_{36}H_{30}P_2Cl_2Pd\cdot 1.5CH_2Cl_2$: C,54.31; H, 4.01. Found: C, 53.81; H, 4.27%.

Preparation of $\mathbf{PtCl_2(1,8\text{-dpmn})\cdot 3H_2O}$ 2·3H$_2$O. To a solution of $PtCl_2(cod)$ (59 mg, 0.16 mmol) in CH_2Cl_2 (5 mL), 1,8-dpmn (84 mg, 0.16 mmol) in CH_2Cl_2 (10 mL) was added at room temperature. After stirring for 2 h, the solvent was removed under reduced pressure and the residue was crystallized from CH_2Cl_2 and acetone to give white crystals of **2**$\cdot 3H_2O$ (58 mg, 43%). Anal. calc. for $C_{36}H_{30}P_2Cl_2Pt\cdot 3H_2O$: C, 51.19; H, 4.30. Found: C, 50.56; H, 3.87%.

Preparation of $\mathbf{[Pd(1,8\text{-dpmn})(XylNC)_2](PF_6)_2}$ 3a. To a solution of $PdCl_2(1,8\text{-dpmn})\cdot 1.5CH_2Cl_2$ (100 mg, 0.12 mmol) in CH_2Cl_2 (10 mL), XylNC (33 mg, 0.25 mmol) in CH_2Cl_2 (10 mL) and NH_4PF_6 (98 mg, 0.60 mmol) in acetone (10 mL) was added at room temperature. After stirring for 2 h, the solvent was removed to dryness and the residue was extracted with CH_2Cl_2. Recystallization from CH_2Cl_2 and diethyl ether gave pale yellow crystals of **3a** (137 mg, 87%) (contained CH_2Cl_2 as a solvated molecule). IR (Nujol): 2213 (N≡C), 835 (PF_6) cm^{-1}. ^1H NMR(CD_3COCD_3): δ 1.97 (s, *o*-Me, 12H), 4.60 (center of an AB quartet, $J_{HH} = 10.0$ Hz, 4H, CH_2), 5.27 (s, CH_2Cl_2), 5.6–8.2. ^{31}P NMR ($CDCl_3$): δ 30.1 (s), −143.4 (sep., $J_{PF} = 707$ Hz). Anal. Calc. for $C_{54}H_{48}N_2P_4F_{12}Pd\cdot 1.5CH_2Cl_2$: C, 50.86; H, 3.92; N, 2.13. Found: C, 50.44; H, 3.65; N, 1.99%.

Preparation of $\mathbf{[Pd_2(1,8\text{-dpmn})(XylNC)_4](PF_6)_2}$ 6a. To a solution of $[Pd_2(XylNC)_6](PF_6)_2$ (100 mg, 0.08 mmol) in CH_2Cl_2 (10 mL) was added 1,8-dpmn (43.6 mg, 0.08 mmol) in CH_2Cl_2 (5 mL) at room temperature. After stirring for 2 h, the solvent was removed to dryness and the residue was extracted with benzene. Recystallization of the residue from CH_2Cl_2 and diethyl ether gave yellow crystals of **6a** (71 mg, 57%) (contained CH_2Cl_2 as a solvated molecule). IR (Nujol): 2187 (w), 2160 (st.) (N≡C), 837 (PF_6) cm^{-1}. UV-vis (CH_2Cl_2): λ_{max} 385 nm. ^1H NMR (CD_3COCD_3): δ 2.11 (s, *o*-Me, 6H), 2.21 (s, *o*-Me, 6H), 2.30 (s, *o*-Me, 6H), 2.38 (s, Me, 6H), *ca.* 4.1, *ca.* 4.8, *ca.* 5.2, *ca.* 5.5 (b, CH_2, 1H), 6.8–7.8. $^{31}P\{^1H\}$ NMR (CD_3COCD_3): δ 21.3 (d, $^2J_{PP'} = 54.5$ Hz), 13.4 (d, $^2J_{PP'} = 54.5$ Hz), −143.4 (sep., $^1J_{PF} = 710$ Hz). Anal. calc. for $C_{72}H_{66}N_4P_4F_{12}Pd_2\cdot 0.5CH_2Cl_2$: C, 54.61; H, 4.24; N, 3.51. Found: C, 54.35; H, 4.21; N, 3.53%.

Preparation of $\mathbf{[Pd_2(1,8\text{-dpmn})(MesNC)_4](PF_6)_2}$ 6b. Yellow crystals (56%) of **6b**, recrystallized from acetone and diethyl ether, were obtained from $[Pd_2(MesNC)_6](PF_6)_2$ and 1,8-dpmn, according to a procedure similar to that for **6a**. IR (Nujol): 2189 (w), 2162 (st.) (N≡C), 837 (PF_6) cm^{-1}. UV-vis. (CH_2Cl_2): λ 385 nm. ^1H NMR (CD_3COCD_3): δ 2.02 (s, Me, 3H), 2.08 (s, Me, 6H), 2.15 (s, Me, 6H), 2.22 (s, Me, 9H), 2.3 (s, Me, 12H), 3.88–5.15 (m, CH_2, 4H), 5.6–8.2. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 21.2 (d, $^2J_{PP'} = 54.5$ Hz), 12.4 (d, $^2J_{PP'} = 54.5$ Hz), −143.4 (sep., $^2J_{PF} = 710$ Hz). Anal. calc. for $C_{76}H_{74}N_4P_4F_{12}Pd_2\cdot (CH_3)_2CO$: C, 56.95; H, 4.84; N, 3.36. Found: C, 57.09; H, 4.81; N, 3.34%.

Preparation of $\mathbf{[Pt_2(1,8\text{-dpmn})(XylNC)_4](PF_6)_2}$ 7a. 1,8-Dpmn (20 mg, 0.038 mmol) was added to a solution of $[Pt_2(XylNC)_6](PF_6)_2$ (50 mg, 0.034 mmol) in acetone (10 mL mL) at room temperature and stirred for 2 h. The solvent was concentrated to *ca.* 3 mL and diethyl ether was extracted with benzene. Recrystallization of the residue from acetone and diethyl ether gave pale yellow crystals of **7a** (38 mg, 65%). IR (Nujol): 2202 (w), 2164 (st) (N≡C), 835 (PF_6) cm^{-1}. ^1H NMR (CD_3COCD_3): δ 2.13 (s, *o*-Me, 6H), 2.22 (s, *o*-Me, 6H), 2.24 (s, *o*-Me, 6H), 2.37 (s, *o*-Me, 6H), 4.38 (c, CH_2, 2H), 5.45 (c, CH_2, 2H), 6.8–7.9 (m, Ph, 54H). $^{31}P\{^1H\}$ NMR(CD_3COCD_3): δ 9.17 ($^1J_{P'Pt} = 3076$ Hz, $^2J_{P'Pt} = 53$ Hz, $^2J_{PP'} = 25$ Hz), 28.0 ($^1J_{P'Pt} = 2275$ Hz, $^2J_{P'Pt} = 440$ Hz, $^2J_{PP'} = 25$ Hz), −143.4 (sep. $^1J_{PF} = 710$ Hz). Anal. calc. for $C_{72}H_{66}N_4P_4F_{12}Pt_2$: C, 50.02; H, 3.85; N, 3.24. Found: C, 50.90; H, 4.00; N, 3.09%.

Preparation of $\mathbf{[Pt_2(1,8\text{-dpmn})(MesNC)_4](PF_6)_2}$ 7b. Pale yellow crystals of **7b** (72%) were prepared from the reaction of $[Pt_2(MesNC)_6](PF_6)_2$ with 1,8-dpmn. IR (Nujol): 2206 (w), 2170 (st) (N≡C), 835 (PF_6) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.79, 1.99, 2.02, 2.19 (s, *o*-Me, 24H), 2.17, 2.26, 2.30, 2.43 (s, *p*-Me, 12H), 4.20, 4.93 (c, PCH_2, 4H), 6.0–7.7 (m, Ph, 34H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 8.90 ($^1J_{PPt} = 3070$ Hz, $^2J_{PPt} = 50$ Hz, $^2J_{PP'} = 25$ Hz), 26.8 ($^1J_{P'Pt} = 2272$ Hz, $^2J_{P'Pt} = 450$ Hz, $^2J_{P'P} = 25$ Hz), −143.6 ($^1J_{PF} = 707$ Hz). Anal. calc. for $C_{76}H_{74}N_4P_4F_{12}Pt_2$: C, 51.13; H, 4.18; N, 3.14. Found: C, 52.10; H, 4.43; N, 2.99%.

Preparation of $\mathbf{[Pd_2(1,8\text{-dpmn})_2(MesNC)_2](PF_6)_2}$ 8b. To a solution of **4b** (86 mg, 0.06 mmol) in acetone (10 mL) was added 1,8-dpmn (72 mg, 0.13 mmol) at room temperature. After stirring for 2 h, the solvent was removed *in vacuo* and the residue was extracted with acetone. Reddish orange complex **8b** (30 mg, 55%) was isolated by recrystallization from acetone–diethyl ether. IR (Nujol): 2133 (N≡C), 838 (PF_6) cm^{-1}. UV-vis (CH_2Cl_2): λ_{max} 460 nm. ^1H NMR ($CDCl_3$): δ 1.72 (s, *o*-Me, 12H), 2.44 (s, *p*-Me, 6H), 4.20, 3.8–5.9 (c, PCH_2, 8H), 6.6–8.1 (m, Ph, 56H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 22.16 ($^2J_{P1P2} = -75$ Hz, $^2J_{P1P2'} = 60$ Hz, $^3J_{P1P1'} = 264$ Hz), 9.09 ($^1J_{P2P1} = -75$ Hz, $^3J_{P2P2'} = 17$ Hz, $^3J_{P2P1'} = 60$ Hz), −143.6 ($^1J_{PF} = 707$ Hz). Anal. calc. for $C_{92}H_{82}N_2P_6F_{12}Pd_2$: C, 59.98; H, 4.49; N, 1.52. Found: C, 59.65; H, 4.18; N, 1.43%.

Preparation of $\mathbf{[Pd_2(1,8\text{-dpmn})_2(XylNC)_2](PF_6)_2}$ 8a. Reddish orange complex **8a** (55%) was prepared from the reaction of $[Pd_2(XylNC)_6](PF_6)_2$ with 1,8-dpmn according to a similar procedure to **8b**. IR (Nujol): 2132 (N≡C), 841 (PF_6) cm^{-1}. UV-vis (CH_2Cl_2): λ_{max} 463 nm. ^1H NMR (CD_3COCD_3): δ 1.79 (s, *o*-Me, 12H), 3.74–5.90 (b, CH_2, 8H), 6.2–8.0. $^{31}P\{^1H\}$ NMR (CD_3COCD_3): δ *ca.* 19.0 (c), *ca.* 9.0 (c), −144.4 (sep. $^1J_{PF} = 710$ Hz). Anal. calc. for $C_{90}H_{78}N_2P_6F_{12}Pd_2\cdot 0.5CH_2Cl_2$: C, 58.54; H, 4.29; N, 1.15. Found: C, 58.68; H, 4.29; N, 1.31%.

Preparation of $\mathbf{[Pt_2(1,8\text{-dpmn})_2(XylNC)_2](PF_6)_2}$ 9a. To a solution of **5a** (50 mg, 0.034 mmol) in acetone (10 mL) was added 1,8-dpmn (37 mg, 0.07 mmol) at room temperature. After stirring for 2 h, the solvent was removed *in vacuo* and the residue was extracted with acetone. Recrystallization from acetone–diethyl ether gave yellow crystals of **9a** (17 mg, 25%). IR (Nujol): 2152 (N≡C), 841 (PF_6) cm^{-1}. UV-vis (CH_2Cl_2): λ_{max} 461 nm. ^1H NMR (CD_3COCD_3): δ 1.80 (s, *o*-Me, 12H), 4.2–5.90 (b, CH_2, 8H), 6.2–8.0. Anal. calc. for $C_{90}H_{78}N_2P_6F_{12}Pt_2$: C, 54.28; H, 3.95; N, 1.41. Found: C, 54.58; H, 4.00; N, 1.66%.

Preparation of $\mathbf{[Pt_2(1,8\text{-dpmn})_2(MesNC)_2](PF_6)_2}$ 9b. Pale yellow crystals (49%) of **9a** recrystallized from acetone and diethyl ether, were obtained from $[Pd_2(MesNC)_6](PF_6)_2$ and 1,8-dpmn, according to a similar procedure to **9b**. IR (Nujol): 2154 (N≡C), 837 (PF_6) cm^{-1}. UV-vis (CH_2Cl_2): λ 463 nm. ^1H NMR (CD_3COCD_3): δ 1.77 (s, *o*-Me, 12H), 2.86 (s, *p*-Me, 6H), 4.2–5.90 (b, CH_2, 8H), 6.2–8.0. Anal. calc. for $C_{92}H_{82}N_2P_6F_{12}Pt_2$: C, 54.71; H, 4.09; N, 1.39. Found: C, 54.38; H, 4.20; N, 1.55%.

Preparation of $\mathbf{[\{Pd(1,8\text{-dpmn})(XylNC)_2\}\{HN(CH_2)_2(CMe_2)_2CO\}_2](PF_6)_4}$ 10a. To a solution of $[Pd_2Cl_2(XylNC)_4]$ (48 mg, 0.059 mmol) in acetone (10 mL) was added 1,8-dpmn (72 mg, 0.13 mmol) and NH_4PF_6 (100 mg, 0.61 mmol) at room temperature and the mixture was stirred for 24 h. After the solvent was removed *in vacuo*, the residue was extracted with CH_2Cl_2. Recrystallization from CH_2Cl_2 and diethyl ether gave

Table 5 Crystal data for *cis*-$PdCl_2$(1,8-dpmn)·CH_2Cl_2 **1**·CH_2Cl_2, *cis*-$PtCl_2$(1,8-dpmn)·CH_2Cl_2 **2**·CH_2Cl_2, [Pd_2(1,8-dpmn)$(MesNC)_4$]$(PF_6)_2$· $(CH_3)_2CO$ **6b**·$(CH_3)_2CO$, [Pt_2(1,8-dpmn)$(MesNC)_4$]$(PF_6)_2$ **7b**, [Pd_2(1,8-dpmn)$_2$$(MesNC)_2$]$(PF_6)_2$·2$(CH_3)_2CO$ **8b**·2$(CH_3)_2CO$ and [{Pd(1,8-dpmn)$(XylNC)_2$}{$HN(CH_2)_2(CMe_2)_2CO$}$_2$]$(PF_6)_4$ **10a**

	1·CH_2Cl_2	**2**·CH_2Cl_2,	**6b**·$(CH_3)_2CO$	**7b**	**8b**·2$(CH_3)_2CO$	**10a**
Formula	$C_{37}H_{32}P_2Cl_4Pd$	$C_{37}H_{32}P_2Cl_4Pt$	$C_{79}H_{80}N_4OF_{12}P_4Pd_2$	$C_{76}H_{74}N_4F_{12}P_4Pt_2$	$C_{98}H_{94}N_2F_{12}O_2P_6Pd_2$	$C_{72}H_{84}N_4O_2P_6F_{24}Pd$
Molecular weight	786.8	875.5	1666.2	1785.5	1958.46	1785.69
Color	Pale yellow	White	Yellow	Pale yellow	Orange	Pale yellow
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1$ (no. 4)	$P2_1$ (no. 4)	$C2/c$ (no. 15)	$P\bar{1}$ (no. 2)
a/Å	14.414(2)	14.45(1)	10.919(6)	11.06(5)	27.18(2)	15.660(4)
b/Å	9.871(2)	9.898(2)	25.859(9)	25.823(10)	18.653(3)	23.72(1)
c/Å	24.796(4)	24.74(1)	14.502(9)	14.292(10)	25.17(2)	11.793(4)
a/°						101.72(4)
β/°	101.87(1)	101.72(6)	108.13(5)	108.1(1)	124.42(5)	91.57(3)
γ/°						105.34(3)
v/Å^3	3453(1)	3464(6)	3891(3)	3881(12)	10527(10)	4120(2)
Z	4	4	2	2	4	2
D_{calc}/g cm^{-3}	1.513	1.679	1.422	1.53	1.236	1.439
μ/cm^{-1}	9.59	45.2	6.19	37.4	4.89	4.41
Scan rate/° min^{-1}	16	16	8	8	16	16
No. of reflections ($< 2\theta$)	6456 (<50°)	6488 (<50°)	7413 (<50°)	13652 (<50°)	6998 (<45°)	13161 (<50°)
No. of data ($I > 3.0\sigma(I)$)	2162 ($I > 3.0\sigma(I)$)	1842($I > 3.0\sigma(I)$)	7343 ($I > -10.0\sigma(I)$)	3887 ($I > 2.0\sigma(I)$)	3018 ($I > 3.0\sigma(I)$)	3198($I > 2.5\sigma(I)$)
No. of variables	382	212	895	411	520	482
R; R_w	0.071; 0.075[a]	0.062; 0.061[a]	0.233; 0.231[b]	0.120: 0.167[b]	0.072; 0.086[a]	0.108; 0.128[a]
$R1$			0.101 (for 3493 refs)[b]	0.078 (for 3887 refs)[b]		
GOF[c]	1.73	1.23	1.34	1.40	2.68	1.81

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ ($w = 1/\sigma^2(F_o)$). [b] $R = \Sigma(F_o^2 - F_c^2)/\Sigma F_o^2$, $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $I > 2.0\sigma(I)$ data. [c] GOF = $[\Sigma w(|F_o| - |F_c|)^2/\Sigma(N_o - N_v)]^{1/2}$, where N_o = number of data, N_v = number of variables.

yellow crystals (135 mg, 64.1%) of **10a**. IR (Nujol): 3198, 3135 (N–H), 2218 (N≡C), 1725 (C=O), 847 (PF_6) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.69 (s, Me, 24H), 1.99 (s, *o*-Me, 12H), 2.87 (s, CH_2, 8H), 4.63, 5.86 (c, PCH_2, 4H), 6.7–8.2 (m, Ph, 32H). ^{31}P NMR ($CDCl_3$): δ 30.3 (s), −143.1 (sep., PF_6). Anal. calc. for $C_{72}H_{84}N_4O_2P_6F_{24}Pd$: C, 48.43; H, 4.74; N, 3.14. Found: C, 48.11; H, 4.55; N, 2.97%.

Each cationic compound, $[Pd(XylNC)_2(1,8\text{-dpmn})](PF_6)_2$ and $[HN(CH_2)_2(CMe_2)_2CO](PF_6)$ can be separately isolated by several recrystallizations.

Photochemical reaction of $[Pd_2(1,8\text{-dpmn})_2(XylNC)_2](PF_6)_2$ 8a in CH_2Cl_2

A solution of **8a** (50 mg, 0.028 mmol) in CH_2Cl_2 (10 mL) was irradiated with sunlight. After 3 h, the solvent was removed and the residue was crystallized from CH_2Cl_2 and diethyl ether to give yellow crystals of $[PdCl(1,8\text{-dpmn})(XylNC)](PF_6)$ (45 mg, 85%). IR (Nujol): 2001 (N≡C), 845 (PF_6) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.83 (s, *o*-Me, 6H), 3.82, 5.40 (c, PCH_2, 4H), 6.2–8.0 (m, Ph, 28H). ^{31}P NMR ($CDCl_3$): δ 32.1 (d, $J_{PP} = 35.4$ Hz), 32.6 (d, $J_{PP} = 35.4$ Hz), −143.1 (sep., $J_{PF} = 710$ Hz, PF_6). Anal. calc. for $C_{45}H_{39}NClP_3F_6Pd$: C, 57.34; H, 4.17; N, 1.49. Found: C, 57.26; H, 3.95; N, 1.35%.

Data collection

Complexes, **1**·CH_2Cl_2, **2**·CH_2Cl_2 **6b**·$(CH_3)_2CO$, **7b**, **8b**·2$(CH_3)_2CO$ and **10a**, were recrystallized from CH_2Cl_2–diethyl ether. Cell constants were determined from 20–25 reflections on a Rigaku four-circle automated diffractometer AFC5S. The crystal parameters along with data collections are summarized in Table 5. Data collection was carried out by a Rigaku AFC5S refractometer at 27 °C. Intensities were measured by the 2θ–ω scan method using Mo-Kα radiation ($\lambda = 0.71069$ Å). Throughout the data collection the intensities of three standard reflections were measured every 200 reflections as a check of the stability of the crystals and no decay was observed. Intensities were corrected for Lorentz and polarization effects. The absorption correction was made with the ψ scan method. Atomic scattering factors were taken from Cromer and Waber, the usual tabulation.[26] Anomalous dispersion effects were included in F_{calc};[27] the values of $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[28] All calculations were performed using the TEXSAN crystallographic software package.[29]

Determination of the structures. All structures except **1**·CH_2Cl_2, **2**·CH_2Cl_2 and **8b**·2$(CH_3)_2CO$ (solved by Direct methods) were solved by Patterson methods (DIRDIF92, PATTY).[30] The positions of all nonhydrogen atoms except nonhydrogen atoms from the CH_2Cl_2 solvent for **1**·CH_2Cl_2 and six F atoms for **8b**·2$(CH_3)_2CO$, were refined with anisotropic thermal parameters by using full-matrix least-squares methods. The positions of all nonhydrogen atoms except the Pt, Cl and P atoms for **2**, and the Pt and P atoms for **7b** were refined with isotropic thermal parameters by using full-matrix least-squares methods. The positions of all nonhydrogen atoms of **6b**·$(CH_3)_2CO$ were refined with anisotropic thermal parameters by using full-matrix least-squares methods. The positions of the Pd, P and two N atoms for **10a** were refined anisotropically and other nonhydrogen atoms were refined isotropically. All hydrogen atoms were calculated at the ideal positions with the C–H distance of 0.95 Å and not refined.

CCDC reference numbers 157470, 157471 and 161769–161772.

See http://www.rsc.org/suppdata/dt/b1/b100860i/ for crystallographic data for **6b**·$(CH_3)_2CO$ (157470) and **7b** (157471) in CIF or other electronic format.

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